Development, adaptation and testing of remote, non-powered sampling systems for temporal characterization of hydraulically fractured shale systems

by

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Abstract:

Extraction of natural gas from shale formations using the process of hydraulic fracturing (fracking) requires the use of thousands of cubic meters of fluid. Hydraulic fracturing fluids are pumped under pressure into shale formations, fracturing the shale and releasing pockets of trapped gases. When the pressure in a natural gas well is released, the previously trapped gases flow to the surface and are collected. As much as 80% of the fracking fluids return to the surface as well. These fluids, known as flow-back fluids or produced water, contain high concentrations of shale minerals including heavy metals and radionuclides. They also serve as a medium for microbial communities which produce hydrogen sulfide and other corrosive compounds. The storage, transportation and treatment of flow-back fluids increase the cost of natural gas production, and present an environmental health risk to local surface water systems. Further study of these fluids is required to constrain the process by which shale constituents are mobilized during hydraulic fracturing.

A fundamental component of any attempt to characterize the chemistry and microbiology of hydraulic fracturing fluids is effective sample collection. Even in ideal conditions, sampling these fluids consistently and with high frequency can be logistically difficult. Often periodic sampling, or spot sampling, is infrequent, occurring on the order of days to weeks. Spot samples offer a glimpse of fluid chemistry and microbiology at specific time-points, and can indicate that changes are occurring, but deliver little insight into the timescale or mechanisms of those changes. High resolution sampling, on the order of hours, has revealed that large changes in aquatic chemistry can occur on short timescales. In river systems, spot sampling has been shown to miss large volumes of nutrient influx as a result of heavy

precipitation resulting in an underestimation of the concentration of these nutrients in the system. Once in the river, these nutrients are consumed and modified by microorganisms. Similarly, production rates of hydraulic fracturing fluids from natural gas wells are not constant and current spot sampling regimes may be missing changes in the fluids that are occurring on short timescales.

The purpose of this project was to build and test continuous, remote sampling systems for use in characterizing chemical and microbial changes in hydraulic fracturing fluids. To accomplish this, I adapted a design known as the osmosampler that has been used successfully in deep ocean research. Osmosamplers function entirely by osmotic pressure generated by separating a chamber of concentrated salt water from a chamber of deionized water. This pressure is used to collect a sample of fluid in a long coil of small diameter Teflon tubing. Upon retrieval of the sampler, the tubing is divided into sections that contain fluids sampled at different time points throughout the deployment. Analysis of these sections provides a high-resolution dataset regarding changes in fluid conditions over time. For this project, I constructed three samplers, one based on those used in deep ocean applications using rigid cartridge membranes, and two of my own design using thin film forward osmosis membranes.

For 58 days, the samplers collected fluid out of a flask full of D.I. water that was periodically spiked with NaCl and fluorescent microspheres. After each addition, reference samples were collected from the flask using a pipette, and stored. The conductivity data, indicating the concentration of total dissolved solids collected from two of the samplers, closely matched the reference samples though on different timescales. The samplers using the thin film membranes pumped very quickly, one reaching capacity after only a few days and the

other after a few weeks. Data retrieved from these samplers was not complete for the 58 days, but the subset of data they did collect was accurate when compared to the spot sample data. The sampler using the cartridge membranes pumped very slowly and did not reach capacity within the 58 day experiment. Data from this sampler did not accurately reflect changes in the reservoir fluid conditions due to an unpredictably variable pumping rate throughout the trial.

This study will help to inform design choices for future osmosamplers to be deployed in the field. These samplers show great potential for use in characterizing the chemistry and microbiology of hydraulic fracturing fluids, as well as other aqueous environments. Further testing is required to ensure that the thin film samplers can withstand the harsh environment present in hydraulic fracturing fluids.

Introduction:

Overview

Hydraulic fracturing (fracking) as a method for natural gas extraction in deep geological strata has received significant attention in recent years from drilling companies, politicians, the media and concerned citizens. The practice of fracking has made available vast, previously inaccessible reserves of methane.[1] This fuel has been heralded in the United States as an abundant domestic source of energy and as a cleaner burning alternative to oil. Despite the potential economic and geopolitical benefits, hydraulic fracturing has received considerable negative attention due to concerns related to water contamination.

In order to access the natural gas contained within shale formations, a well is drilled vertically into the formation, often at a depth of 1000m or greater.[1] Additional bores are then

drilled horizontally, radiating outward from the vertical well to access more of the gas-rich shale. After the well has been cased with steel and concrete, sections if the casings are perforated using explosives.[1] As much as 18,000 cubic meters (4.75 million gallons) of fracking fluid is then injected into this well under high pressure to fracture the shale and release the gas contained.[1] At depth, the drilling fluid interacts with the shale and mobilizes dissolved solids such as chloride and radionuclides in high concentrations.[1,2,3] When the pressure is released to allow the gas to travel to the surface, thousands of cubic meters of this fluid also come to the surface.[1] This fluid is known as produced water.

Recent studies have demonstrated a connection between produced water from fracking operations and surface water contamination.[2,3] The Effluent from wastewater treatment facilities which process hydraulic fracturing produced water has been shown to increase downstream radon and chloride concentrations.[2,3] The process by which shale constituents become mobilized in the fracking fluids is poorly understood.[4,5] Further research utilizing improved sampling techniques is needed to constrain the processes by which these solids become mobile in fracking fluids. This study looks at the potential to adapt the osmosampler design to obtain high temporal resolution data regarding changes in hydraulic fracturing fluid chemistry and microbiology.

Importance of Fracking

Globally, tight shale formations (those which require the use of hydraulic fracturing for natural gas extraction) are projected to contain as much as 204 trillion cubic meters of technically recoverable natural gas.[6] This is enough to meet the global demand for natural gas

for 60 years at the current rate of consumption.[7,8] Between 1990 and 2012, extraction of natural gas from shale formations in the United States increased from 4.8 billion cubic meters to 275 billion cubic meters per year.[6] In 2012, natural gas provided 27% of all energy consumed in the United States, 34% of which was extracted from tight shales through hydraulic fracturing.[9] By 2040, shale gas is projected to provide 50% of all natural gas and 15% of the total energy consumed in the United States.[10] This rapid increase in domestic oil and natural gas production is a direct result of developments in extraction technology, namely the processes of hydraulic fracturing and horizontal drilling.

Hydraulic fracturing was first utilized to access gas in the Barnett shale formation in Texas and Oklahoma.[1] In the last decade, fracking wells have been drilled into shale formations in 17 states.[1] The Marcellus Shale, which underlies much of Pennsylvania, New York, Ohio and West Virginia, is estimated to contain as much as 14 trillion cubic meters of natural gas[1] and could be the second largest reservoir of natural gas in the world.[11] The low permeability of the formation, on the order of 10^{-6} millidarcies, made gas extraction infeasible in the Marcellus Shale until the use of hydraulic fracturing technologies became widespread.[12] As a result, per well production of natural gas from the Marcellus shale increased from approximately 2.8×10^{7} cubic meters per day to nearly 4.5×10^{8} cubic meters per day in between 2007 and the present.[13] There are currently around 7,000 wells in Pennsylvania. Under a medium development scenario, this number is projected to exceed 60,000 by 2030.[14]

Composition of Flowback Fluids

Composition of the drilling fluid used for fracking operations varies between companies and well sites. Generally, ninety percent of the fluid by volume is comprised of fresh water and nine percent is comprised of proppants, typically sand, used to hold fractures open. The remaining one percent is composed of a mixture of 750 possible chemicals.[15] including surfactants, acids and detergents to improve extraction efficiency, and biocides to minimize biofouling.[1] Depending on the specific extraction method used and geologic formation, 10% to 80% of this fluid returns to the surface as flow-back fluid when the well pressure is released.[1]

Flow-back fluids contain high concentrations of ions such as Cl^-, Br^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} and Ba^{2+}, and radionuclides such as Sr-87, Ra-226 and Ra-228, which were not present in the initial drilling fluids.[1,7] Total dissolved solids (TDS) in flow-back can range from 800 mg/l to 300,000 mg/l, approximately 6.5 times the concentration found in seawater[16] and 500 times the concentration found in freshwater.[3] Storage, treatment and disposal of radioactive and high TDS fluids pose a challenge to drilling companies, and present a significant environmental health risk.[3,14,1]

In many regions, flow-back fluids are stored onsite until they can be disposed of by injection into deep storages wells. However, due to the unstable geology underlying Pennsylvania, few storage wells exist in the state.[14] Previously, flow-back fluids in Pennsylvania were diverted through municipal water treatment plants. These facilities proved incapable of effectively treating fracking waste.[14] Subsequent regulations have limited treatment to industrial wastewater treatment facilities which are designed to handle brines from oil and gas drilling. As a result of these regulations, the treatment of wastewater for reuse as drilling fluid

for another well has become a common practice.[17] Though the recycling of wastewater has reduced the potential volume of fluids sent to treatment plants, the rapid increase in the number of new wells in Pennsylvania has resulted in a 570% increase in the total wastewater volume generated in the region since 2004.[4] This increase has stressed existing treatment infrastructure.[4] Despite best practices, which remove at minimum 95% of TDS from fracking wastewater, what solids that remain in the effluent from treatment plants have begun accumulating in river sediments.[17]

Many of the potentially problematic solutes found in flow-back fluids are naturally occurring constituents of deep shale formations, but likely exist in a redox state that keeps them bound to the shale.[4] The processes by which these solids become mobile in the fracking fluids are not well understood. Two hypotheses currently exist to explain the mobilization of solids in hydraulic fracturing fluid. One postulates that the fracking fluid itself is responsible for dissolving shale minerals[5], while the other postulates that the drilling fluid mixes pre-existing high TDS brines in the shale.[16] The second hypothesis suggests that hydraulic fracturing fluids are only responsible for transporting solids to the surface that had already been dissolved by fluids in the shale. Currently the only way to sample borehole fluids is at the surface, after mobilization occurs. A long-term continuous sampler capable of deployment in the borehole prior to the injection of the hydraulic fracturing fluids could collect fluids before and after drilling. If brines collected before drilling are highly concentrated with the solutes in question, this would favor the mixing hypothesis. If the solutes do not appear in the sample record until after the introduction of fracking fluids, this would favor the fracking fluid hypothesis. High

resolution, in situ samplers have the potential as a valuable tool in determining the mechanism by which mobilization occurs.

Hydraulic fracturing fluids also provide a medium for microbial growth, a potential means to transport endemic shale microbes to the surface and a vector by which non-endemic microbes are introduced to the fracking shale environment. Studies have shown that microbes have can contribute to mobilization of labile salts and metals in hydraulic fracturing fluid by catalyzing redox reactions.[18] Similar microbe induced reactions occur with metals in drilling equipment resulting in corrosion.[18] The buildup of microbial biofilms can reduce the porosity of the geologic formation and clog drilling equipment.[18] The source of microorganisms in hydraulic fracturing fluids is unclear.[19] Through 16s RNA gene sequencing of the samples in these studies, they found that significant changes occur in the structure of the microbial community over time.[19] Early samples indicate some inital diversity within the microbial community, but later samples become dominated by a small number of taxa, often related to Clostridia.[19] In a 2014 study, Maryam A. Cluff, et al. found that greater than 90% of the community in flowback and produced fluids was related to halotolerant bacteria associated with fermentation, hydrocarbon oxidation, and sulfur-cycling metabolisms, including heterotrophic genera *Halolactibacillus, Vibrio, Marinobacter, Halanaerobium,* and *Halomonas,* and autotrophs belonging to *Arcobacter*.[20]

Sulfur-cycling microbes in the fluids, can produce hydrogen sulfide, “souring” the gas and resulting in a lower quality product[19]. Current assay protocols used by the drilling companies focus on sulfate-reducing bacteria only and do not include those that could produce hydrogen sulfide from other sources of sulfur.[19] Gas companies add biocides to the drilling

fluids to limit growth of these microbes, however, pressure and temperature have been shown to reduce the effectiveness of these chemicals.[19] As a result, drilling companies are selecting for organisms that are resilient to the poison.[21] As fluids produced from natural gas wells travel to the surface they rapidly transition from an anoxic, high temperature, and high pressure environment to an oxygen rich, low temperature, and low pressure environment. In most studies of microbial communities in hydraulic fracturing fluids, the sampling frequency has been low, often at weekly or monthly intervals.[18] Low sampling frequency makes it impossible to accurately quantify the rate of change of the microbial communities, much less driving factors for the changes.[19]

Sampling of hydraulic fracturing fluids

An alternative to spot sampling is the use of autonomous in-situ analyzers. These devices measure certain parameters in a body of water using probes and either record or broadcast this data periodically. An example of this type of system is the TROLL 9500 water quality instrument made by In-Situ Inc. (Ft. Collins, CO), which has a suite of ion selective probes available. Though impressive in their capabilities, these instruments have some significant drawbacks. They are expensive, costing thousands of dollars per unit, they require electrical power, and the analytical capability is limited to the probes that are available.

Another alternative to spot sampling is a system that is capable of collecting samples autonomously with high resolution and storing those samples for analysis at a later date. One device in particular, the osmosampler, has been used for this purpose with great success in oceanographic research for sampling fluids at the seafloor.[22] Designed for extended

deployments, osmosamplers do not require electricity and have no moving parts. Their robust simplicity and ability to provide high-resolution samples make osmosamplers ideally suited for use to characterize chemical and microbiological processes in hydraulic fracturing fluids. This thesis represents the preliminary design, adaptation and testing of osmosamplers for this use. After studying the osmosampler designed for deep ocean research, I developed my own design for use in studying hydraulic fracturing operations. It is my hypothesis that the samplers of my own design can collect and store fluid samples as accurately as the deep ocean samplers.

Osmosampler Theory and Design

Osmosamplers are driven by the osmotic pressure that is generated across a semi-permeable membrane separating a chamber of highly concentrated NaCl solution from a chamber of deionized (DI) water. This process is known as forward osmosis (FO).[23] The chamber of DI water is contiguous with a long coil (50m-1000m) of small diameter (1 - 1.2mm inside diameter) Teflon tubing also pre-filled with DI water (figure 1). As the water in the chamber diffuses across the membrane into the salt solution, a small negative pressure is generated in the Teflon coil. When deployed in an aqueous environment, this negative pressure draws a sample of the fluid into the tubing. Sample collection is slow, but continuous.

The small diameter of the tubing minimizes mixing and the sample moves through the tube with plug-like flow.[23] After deployment, a full coil of tubing contains a continuous record of fluid conditions over the deployment time. Upon retrieval of the sampler, the tubing can be divided into sections containing samples of fluid representative of the environment at the time they were sampled. Analysis of the fluid in these segments offers a snapshot of the aqueous

environment at a single time-point. Just as slices of an ice core can be used to assemble a record of atmospheric changes over time, comparison of the time-points in the sample coil generates a similar record (though on a much shorter timescale) of changes in fluid conditions. Collectively, the individual analysis of each section provides a high-resolution record of fluid chemistry and microbiology over time.

The collection rate of an osmosampler is controlled by three factors, membrane construction, exposed surface area, draw solution concentration and temperature.[23] The first two factors are fixed in the sampler design by selecting a membrane material and surface area that will provide optimum flow rates. Variations in flow rate due to changes in the draw solution concentration are eliminated by building a sampler with salt reservoir large enough to

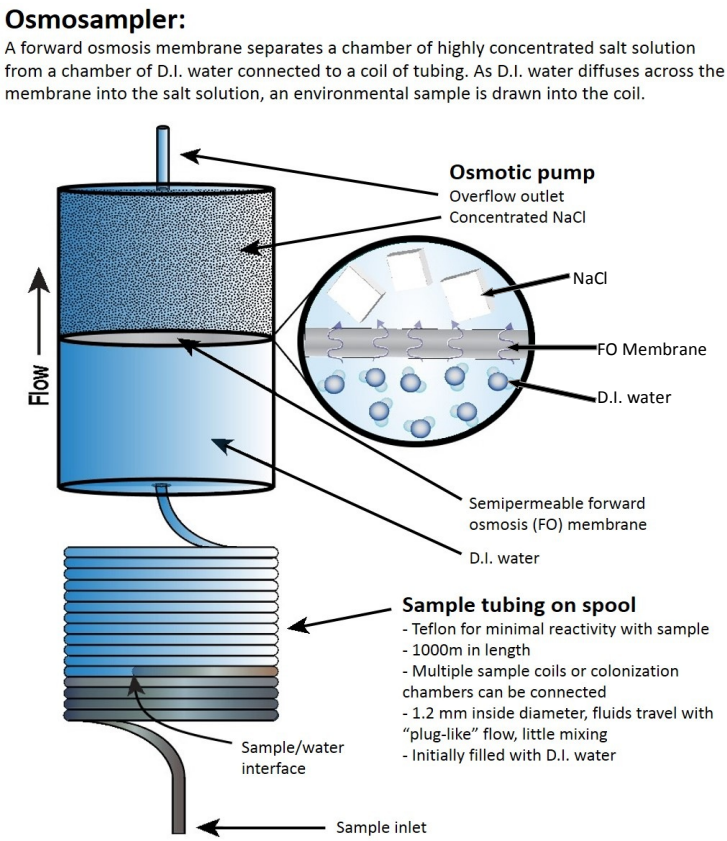

Figure 1: Simplified schematic of an osmosampler

maintain a saturated solution during the deployment period. Environmental temperature will affect the rate of flux across the sampler's membrane, but this effect is predictable.[23] A temperature logger, such as the iButton from Maxim Integrated (San Jose, CA), is deployed with the sampler in the field to account for temperature effect. In addition to allowing for the accurate segmentation of the sample coil, the temperature data itself is useful in understanding possible chemical reactions and factors that shape the structure of microbial communities.

Deep-ocean osmosamplers are designed to be deployed for as long as three years in high-pressure environments. These requirements necessitate the use of highly stable membranes with flow rates as low as 0.1 ml/day.[23] In contrast, the bulk of flow-back waters are produced in the first two weeks of drilling, with smaller volumes of water produced over the lifetime of the well.[1] Effective sampling of flow-back fluid will require samplers with much higher flow rates. This thesis describes the first stages in adapting the oceanographic osmosampler design for use in characterizing the chemical and microbiological conditions of hydraulic fracturing fluid. I developed two osmosamplers using membrane configurations optimized for high flow rates and compared them against a sampler based on the oceanographic design.

Methodology:

Construction of Samplers

The first of the three samplers built for this project was based on the design developed by Dr. Hans Jannasch and his colleagues.[23] This design has become the standard for nearly all osmosamplers used for deep ocean research. The membranes used in this sampler were rigid

cartridge membranes repurposed from medical drug delivery systems. Ten osmotic drug delivery pumps (model #2ML1) were purchased from the Alzet Corporation (Cupertino, CA) and modified for use in the sampler. Because they are intended for drug delivery, these membranes are robust in construction and offer very consistent flow rates from one membrane to another. They also have predictable effects as a result of pressure and temperature changes[24], a characteristic which makes them well suited for use in the deep sea.[22]

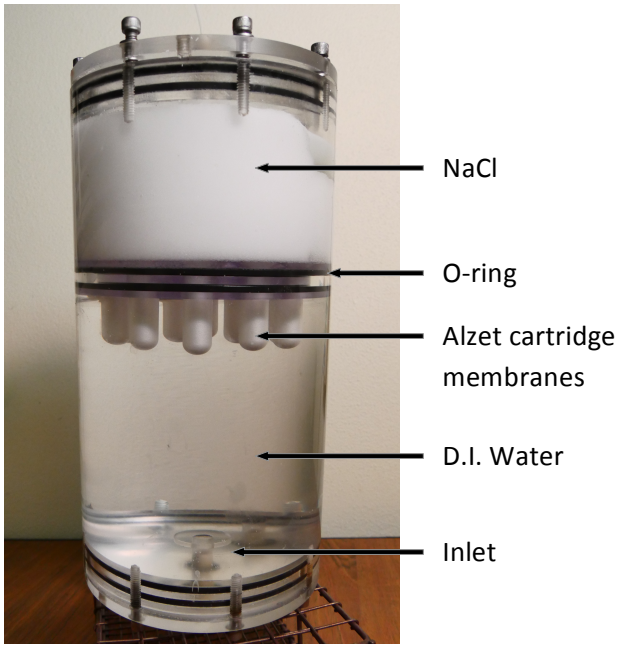

Figure 2: Assembled Alzet pump

One problem that can develop with forward osmosis membranes is a slowing of the flux rate over time as a result of the build-up of ions on the support layer of the membrane[23]. This is known as the external or internal polarization effect, depending on which side of the membranes accumulate ions.[25] The extent to which a membrane is subject to this effect is indicated by a membrane's S-value.[25] A low S-value is indicative of a membrane that has little potential for developing polarization effects and thus offers a consistent flow rate over time.[25] Alzet membranes have a very low S-value respective to other forward osmosis membranes.[23] However, some drawbacks of these membranes are their relatively high cost ($30/membrane) and a low flow rate (.083ml/day/membrane) as compared to other membranes.

The ten cylindrical membranes were separated from their internal drug reservoir using a razor blade affixed to the tool rest of a lathe. Afterwards, the pumps were epoxied using Loctite ES 1902 epoxy (McMaster-Carr #7369A15) into 10 counter-bored holes in an acrylic disc. This disk was slid into an acrylic tube. Double o-rings in grooves around the edge of the disc were used to seal the disc inside the tube. The chamber on one side of the membrane disc was filled with salt and sealed with an end-cap. The chamber on the other side was filled with DI water and then sealed with an identical end-cap. Both acrylic end-caps also used a double o-ring seal and were held in place with stainless steel bolts.

Acrylic was chosen as the material because it has the same expansion coefficient as water, ensuring that the o-ring tolerances will remain consistent with changes in temperature and pressure. Both end-caps were drilled and tapped to accommodate a 1/8-inch flangeless nut (part # p-335) and ferrule (part # p-363r) assembly from IDEX Corp. (Lake Forest, Il.). A 76 meter coil of AWG-17 FEP Teflon tubing from Zeus (Orangeburg, SC) was connected to the DI chamber and a short section of tubing was attached to the salt chamber as an outlet (figure 1).

As osmosamplers cannot be purchased off the shelf, researchers interested in using this technique have to either construct them or have them custom built. Construction of an osmsampler using Alzet membranes requires the use of expensive materials and precision machining. These factors increase their cost and time for construction as the tooling, expertise and time required to machine samplers of this design are resources not often found in microbiology or chemistry labs. The construction of one Alzet sampler for this study cost upwards of $3000. In researching possible alternative construction methods, I adapted the design of parabiotic chambers used to study microorganisms in tissue cultures.[26] Parabiotic

chambers are comprised of two glass tubes separated by a semi-permeable membrane.[26] Two samplers based on this design were constructed using plastic pipe, rather than glass. Most of the materials for these pumps were purchased at a local home improvement store and were assembled using basic tools.

A sample of a novel thin film forward osmosis (FO) membrane was donated from Porifera, Inc (Hayward, CA), a manufacturer of water filtration systems. These particular FO membranes were selected because of their low S-value. Another benefit of these membranes is their low cost (relative to the Alzet membranes) and high flux rate per unit area. The membranes came as paper-thin sheets. Circles were cut from the sheets and epoxied using a 2-part polyurethane (GSP1541-1, GS Polymers, Mira Loma, CA) to a 2-inch ABS pipe drain (part # 845-3P, Sioux Chief Mfg. Co., Peculiar, MO) that was designed to slip inside of a 2-inch acrylonitrile-butadiene-styrene (ABS) pipe. The only difference between the two samplers was the amount of exposed surface area of the membrane. Epoxy was used to seal off sections of the drain, leaving select sections open. The first of these samplers, (FO_1) had all but the center

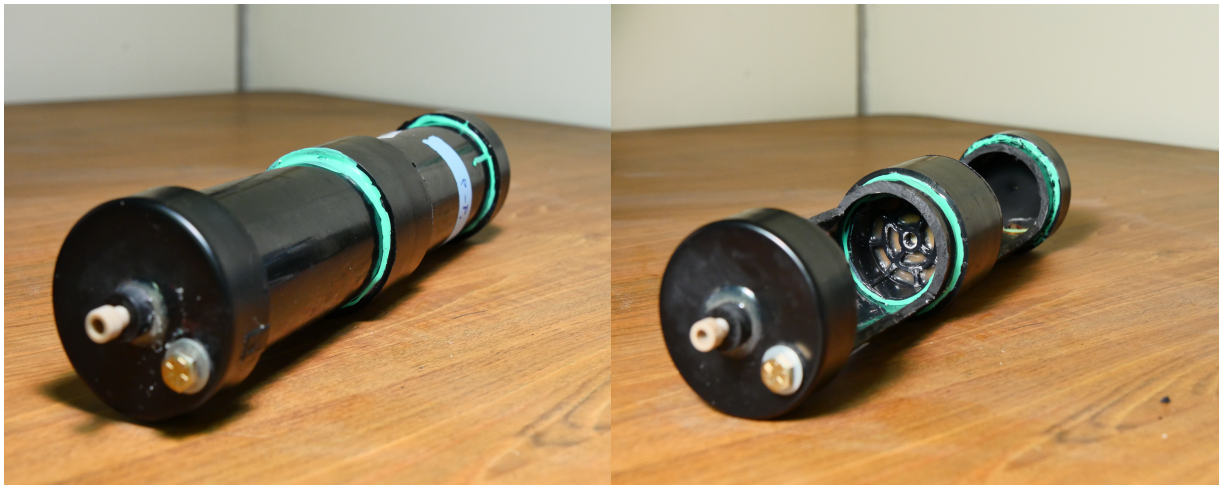

Figure 3: FO pump assembled, and cutaway showing backside of membrane support.

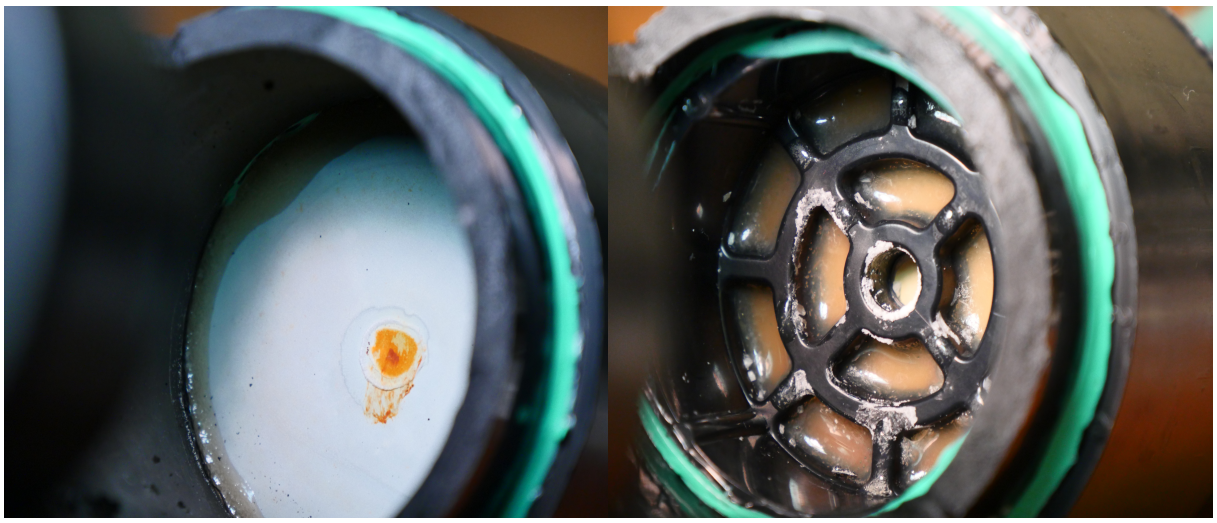

Figure 4: Close-up of the FO_1 sampler membrane (left) and support with epoxy to block holes (right). Note the rust scale build-up on the center of the membrane where diffusion occurs.

hole of the drain blocked off by epoxy (Figure 4) resulting in an exposed membrane surface area of 31.7mm^2. The second, (FO_2) had the center hole and first ring of holes open, with the outer ring block by epoxy. This resulted in an exposed membrane surface area of 185mm^2.

Once the epoxy had cured, the membrane support was cemented using ABS/PVC transition cement (Oatey, Cleveland, OH) into one end of a 6-inch length of 2-inch ABS pipe. A 2-inch ABS pipe cap (part # C5817HD2, NIBCO Inc, Elkhart, IN) was cemented onto the other side of this pipe creating one of the two chambers. This cap had been previously drilled (using a drill press) and tapped for the same 1/8-inch flangeless nut and ferrule assembly from IDEX. The cap was also drilled and tapped for a vent hole, to aid with assembly. This hole was plugged after assembly with a 1/8-inch grade-5 steel bolt and neoprene washer.

The nut and ferrule assembly required an extra piece of ABS be epoxied to the top to provide sufficient depth for the threads. A 2-inch ABS coupler was used to join another 6-inch long section of 2-inch ABS pipe to the membrane side. Another drilled and tapped end-cap with a fitting was cemented to the end of this tube. The DI chambers of the two FO pumps were

each connected to a 76-meter coil of 1.2mm inside diameter Teflon tubing from Zeus. A short piece of tubing was connected to the NaCl chamber of each of the samplers as an outlet.

Experimental Set-Up and Sample Collection

In order to test the long-term flux rates of each of the samplers and their ability to collect, and store fluids from a changing environment, I set-up a side-by-side lab test. The inlet for each of the three samplers was placed into the same reservoir, a 2000mL flask filled with deionized water and green dye (Figure 5). The three samplers collected fluids from the reservoir from July 28th to September 23rd, 2014. Once a week, the reservoir was periodically spiked with 1mL of solution containing 1µm fluorescent microspheres, negatively charged beads that simulate microbial cells treated with fluorescent dye. Twice weekly, the reservoir was spiked with 10g of NaCl to simulate changes in the TDS concentrations found in hydraulic fracturing wastewater. A magnetic stir bar and stir plate were used to keep the solution mixed. After each addition to the reservoir, a 2mL spot sample was taken from the flask as a reference and refrigerated in a sealed test tube. A total of 17 spot samples were collected during the test.

Two of the samplers, the Alzet sampler and FO_1 functioned for the duration of the experiment. Sampler FO_2 was stopped on August 28th when it became clear that the sampler had filled the tube completely and was losing sample into the DI chamber of the pump itself. It was intended that the interface between the green dye and the DI water was to be used to indicate the location of the first sample, but in both FO samplers, green dyed sample had filled the entire tube. The dye/DI interface was used to locate the beginning of the sample in the tubing connected to the Alzet pump. The Teflon tubing connected to the Alzet pump was

divided into 0.6-meter sections. Based on the analysis of the fluids in the sections of Alzet tube and the faster rates of the other two samplers (a single time-point would be represented by a longer section of tubing), the tubing connected to the FO_1 sampler was divided into 1.8-meter sections. The tubing for the FO_2 sampler was divided into 3.2-meter segments. Fluids contained in the segments were expelled into test tubes that were capped and stored in a refrigerator until they were analyzed.

Figure 5: Lab scale experimental apparatus used to test the three samplers. The Alzet sampler (**A**), sampler FO_1 (**B**) and sampler FO_2 (**C**) collected fluid from the reservoir (**D**) into identical coils of Teflon tubing (**E**).

Microsphere Analysis

Microspheres were counted using a Becton Dickinson FACSCaliber flow cytometer (Franklin Lakes, NJ). Initially, we added 25ul of 3um true count beads, as an internal standard, to 500ul of sample and ran this through the flow cytometer. The microsphere concentrations in these first samples were very high. As a result, the flow cytometer may have reported counts that were too low as high density of small spheres can be misinterpreted be the machine as larger particles. To avoid this possibility, subsequent samples were diluted; 25µL of sample was added to 25µL of a solution containing 3µm microspheres and 950µl of DI water. Dilutions of all 17 of the spot samples, were prepared and analyzed using the flow cytometer. The flow cytometer was calibrated using a mixture containing 5µl of a standard 6.0µm true count microsphere solution, 25µl of a standard 1µm microsphere solution, and 25µl of a standard 3µm microsphere solution. Calibration with multiple sizes of microspheres ensures that the flow cytometer can accurately differentiate particles.

Conductivity Analysis

Conductivity was measured using a Thermo Scientific Orion Star A329 portable pH/ISE/Conductivity/ RDO/DO meter with a 013010MD conductivity cell (Waltham, MA). The volume of the spot samples was insufficient to fully submerge the conductivity probe, therefore a 0.5ml aliquot from each of the samples was diluted into 15ml of filtered D.I. water. Conductivity was measured in the diluted samples, and then corrected for the dilution to get actual values. The meter was periodically calibrated using 1413uS/cm and 12.9mS/cm standard solutions from Thermo Scientific.

Results:

Sampler Performance

The sampler built with the Alzet membranes collected sample at a much slower rate than expected, with a mean flux rate of only 0.42mL per day. At this rate, only 20.4 meters of the tubing was filled with sample from the reservoir flask during the test. The Teflon tubing was cut into 34, 0.6m sections. Each section contained approximately 0.6 ml of fluid representing 1.4 days of conditions within the reservoir (Table 1). This is the maximum possible resolution for the sampler as 0.5ml of sample was required for analysis.

Table 1: Characteristics of the three samplers tested that differed by virtue of the membranes used and the surface area of membrane exposed. A 74m sample coil was used and the minimum sample volume was 0.5ml.

Sampler	Membrane	Mean Flux Rate	Sample Capacity	Max. Possible Resolution
Alzet	10 x Alzet 2ML1	0.42ml/day	176 days	1.4 days
FO_1	Porifera FO ($31.7mm^2$)	2.05ml/day	36 days	7.0 hours
FO_2	Porifera FO ($185mm^2$)	12.3ml/day	6.3 days	1.2 hours

Of the two FO samplers, sampler FO_1 had a smaller exposed membrane surface area ($31.7mm^2$) resulting in a mean flux rate of 2.05ml per day. At this rate, with the 76m coil of Teflon tubing attached, this sampler was capable of collecting for approximately 36 days (Table 1). It was allowed to sample for the entire 58 days of the trial, so the first 22 days of sample were lost inside the DI chamber of the pump. As the salt concentration increased in the chamber, it is likely that the flux rates were slightly reduced, but sufficient osmotic pressure

remained to continue sample collection. Within the sample that was preserved in the coil, a 0.6m section represented approximately 7 hours of fluid conditions within the reservoir. Such fine resolution was not needed to track changes that were happening on a bi-weekly timeframe, therefore the coil was divided into 1.8m sections, each representing the average conditions within the flask at 21 hours increments.

FO_2 had approximately 6 times the exposed membrane surface area (185mm^2) as compared to FO_1 resulting in a mean flux rate of 12.3ml per day. At this rate, the 76m Teflon coil was filled in approximately 6.3 days (Table 1). This was not discovered until almost a month into the test. On 8/25/14 the tubing was disconnected, capped and stored in a refrigerator. The sample collected previous to this date was lost inside the pump and the addition of salt to the DI chamber of the pump likely slowed the flux rate over time. With at least 0.5ml of sample required for analysis, the maximum resolution for this sampler is approximately 1.2 hours. This resolution was not needed to track changes on a bi-weekly basis and so the Teflon tubing was divided into 19, 3.6m segments with each segment representing the average fluid conditions within the reservoir at 7.2 hours increments.

Microsphere Count

Unfortunately, a reproducible count of microspheres per sample was difficult to obtain and the resulting data were unreliable. Because the samples only contained 1µm beads and an internal standard of 3µm, the plots produced by the flow cytometer should show only two groupings (on for each size of bead). The plots produced from the reservoir samples were comprised of scattered points with little grouping. Initially we thought this could be attributed

to a high concentration of beads in the samples however, dilution of the samples did not improve the quality of the data. As a result of the weekly additions of highly concentrated microsphere solution, we expected to see a steady increase in the reservoir bead concentration. Both diluted and undiluted flow cytometry datasets show an increase early in the trial followed by a gradual decrease in bead count over time (Figure 6).

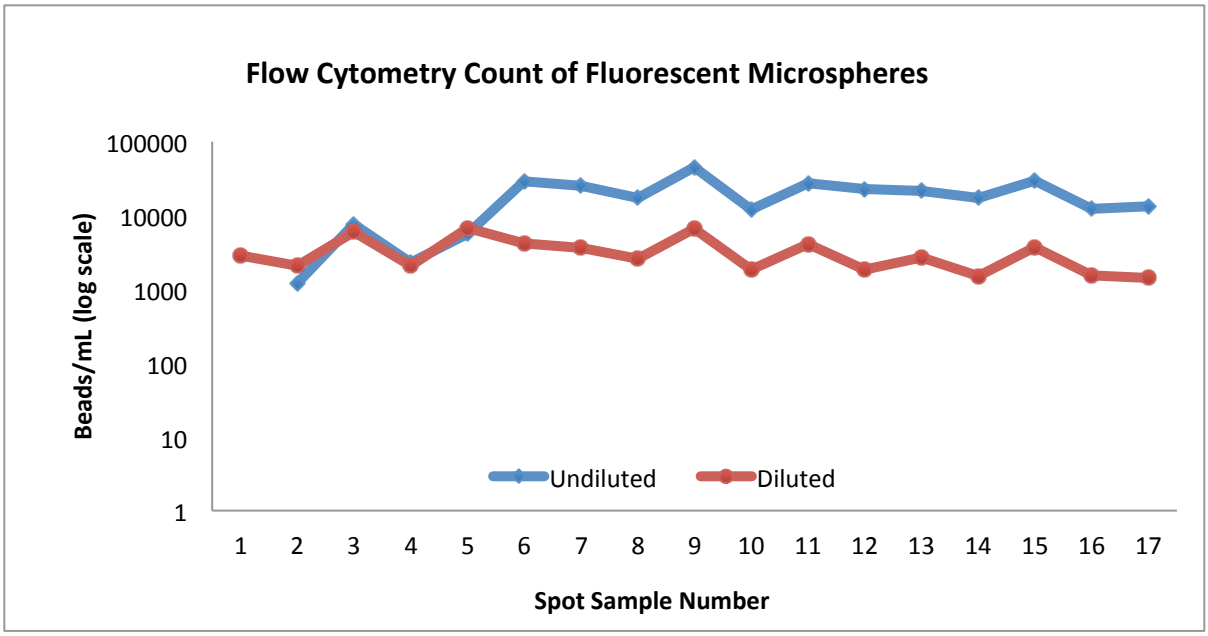

Figure 6: Fluorescent microbead count per spot sample, diluted and undiluted.

Various methods to process the data in order to account for possible causes for these discrepancies only increased variability in the data set. These data could be due to the formation of clumps of microspheres, which are detected as larger particles by the cytometer, or adherence of the beads to the glass of the test reservoir keeping them from being sampled at all.[27] Because of the uncertainty in the microsphere counts and the fact that each run on the flow cytometer consumes sample it was decided to forgo further microsphere measurements in order to conserve sufficient sample volume for conductivity analysis.

Conductivity

Spot samples were collected from the reservoir flask after each addition of salt or microspheres was made. A total of 17 spot samples were collected (figure 7). These samples provide a reference by which to measure the effectiveness of the three osmosamplers. Conductivity values of the spot samples started at 34.98 mS/cm for the first sample and generally increased, with some variation between samples, to 225.2 mS/cm in the last. The linear slope for the spot sample data is 13.74 mS/cm/day with an R^2 value of 0.97. The same amount of salt was added periodically to the reservoir which should have resulted in a spot sample data set which is steadily increasing. It was unexpected to see large spikes in this data

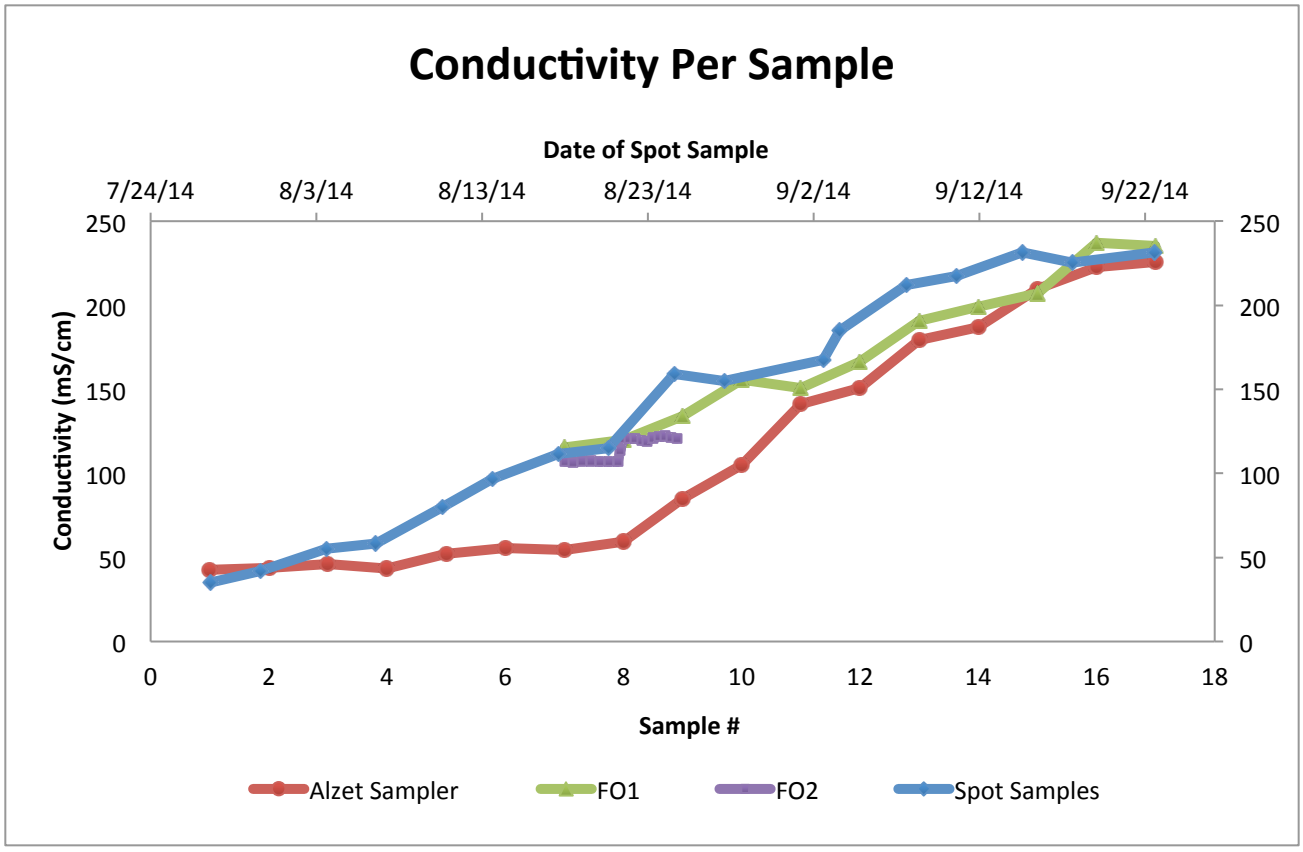

Figure 7: Conductivity data plotted vs. time for side by side comparison of membrane materials and configurations.

and periods of decreasing, rather than increasing, conductivity. One particular spike, at 8/25/14 is likely a result of contamination in the test tube used to store the sample. Particulate matter was observed in the sample in this tube even after a 30:1 dilution. If this data point is removed from the series, the linear R^2 value increases to 0.98.

The Alzet sampler collected the equivalent of 34, 0.6ml samples. After the conductivity values were adjustment by the dilution factor, values were paired and then averaged, creating a data set with 17 equivalent data points to the 17 spot samples. The 17 Alzet sampler data points were plotted by sample number in Figure 7. These data display a long tail in the beginning of the test where the conductivity of the sample remains below 60 mS/cm. Such a tail indicates that the sampler pump very quickly (1.8ml/day) for the first month of the experiment, collecting large volumes in a short period of time and shifting the data by approximately two weeks. After the first month, the sampler seems to slow to a more consistent rate (0.24ml/day) and the data begins to approach the spot samples. As a result, the data makes a sharp increase and approaches, but does not reach the spot sample data until the last sample.

Sampler FO_1 pumped through the entire coil in 36 days. The samples corresponding to approximately 1/3 of the trial were lost inside the pump itself. As a result, the first data point, which provides an important reference for scaling the rest of the data, was eliminated. In order to compare the remaining conductivity data with the spot sample data, the first two retrievable FO_1 samples were used to place the data onto the spot sample timeline. The first two 1.8m sections of tubing closest to the pump had conductivity values of 107.79mS/cm and 113.40mS/cm, respectively. Conductivity for the spot sample taken on 8/18/14 was measured at 111.36mS/cm, so the earliest recoverable sample from the FO_1 was likely recovered around

this date. The average of every four FO_1 samples was taken to form 11 data points, the first of which is plotted as sample 7 on the primary x-axis of Figure 7. This value corresponds to the date 8/18/14. The data from this sampler matches closely with the spot sampler data, though the average rate of change is slightly lower than the spot samples, with an increase of 12.84 mS/cm per data point.

Sampler FO_2 collected fluids at a rate six times faster than FO_1 and similarly lost sample inside the DI chamber of the pump. On 8/25/14 the sample tubing for FO_2 was disconnected from the pump, capped and stored in a refrigerator. This took place before salt was added to the reservoir, so sampler FO_2 does not contain a sample corresponding to this day. This date was used to place the FO_2 conductivity data on the spot sample timeline. Because FO_2 pumped so quickly, a majority of the sample in the tubing represented conditions over the six days prior to 8/25/14.

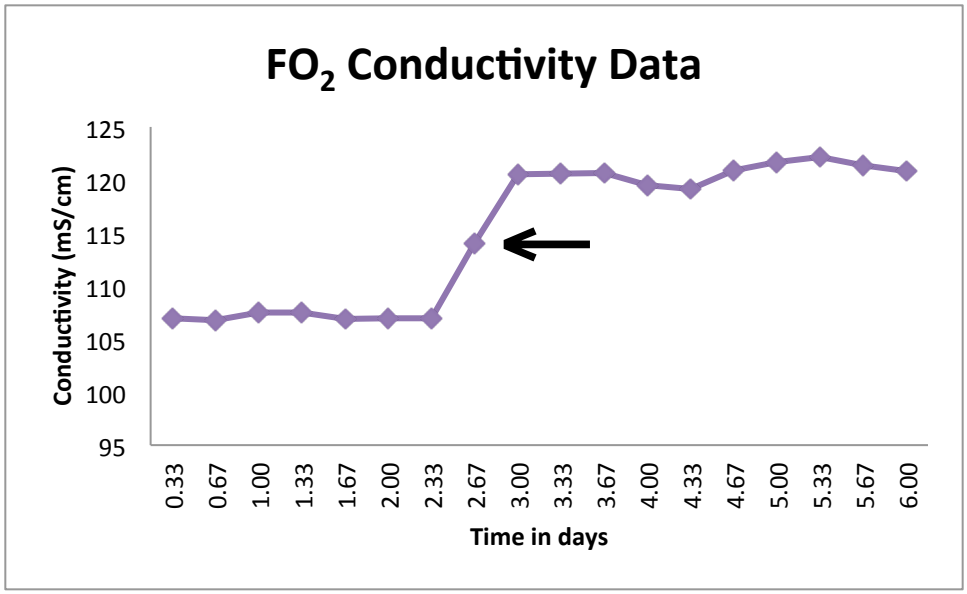

Figure 8: Data from FO_2 plotted as conductivity over elapsed time in days.

Each data point on both Figures 7 and 8 represent the fluid contained in 3.8 meters of the tubing connected to the FO_2 pump. Figure 7 compares data from the FO_2 sampler with data from the Alzet and FO_1 samplers. Figure 8 gives a more detailed view of the FO_2 conductivity data. In this figure, the data is plotted over elapsed time in days. These data represent two discrete time periods, before and after the addition of salt to the reservoir on 8/21/14. As each point in Figure 8 represents the average conductivity in the reservoir over 7.2 hours, the data point in between the two discrete levels likely reflects the change in concentration as the salt was being added to the reservoir (arrow, figure 8).

Discussion:

The overall objective of this study was to experiment with multiple designs of osmosamplers and test their potential to be used to study changes in hydraulic fracturing fluids. To accomplish this, a model hydraulic fracturing fluid reservoir was constructed and the conditions within this reservoir were changed over time. Three separate osmosamplers, using different membranes or exposed membrane surface areas, sampled out of this reservoir simultaneously. The samples collected by the osmosamplers were compared to spot samples taken periodically from the reservoir.

This study provides a proof of concept for the osmosamplers using thin film forward osmosis membranes manufactured by the company Porifera. Both samplers using Porifera membranes completely filled the sample coil and lost early samples into the DI chamber of their respective pumps. However, this is was not a problem inherent to the design, but rather in the period of deployment. Both FO samplers collected fluid samples from the reservoir at

constant flow rates and produced a record that accurately reflects changes in reservoir fluid conditions over time. This test has also proven their capability to sample fluids with a TDS concentration that is within the range of hydraulic fracturing fluids. The conductivity values of the spot samples ranged from 23mS/cm to 231.52mS/cm. Converted to TDS using the equation: (conductivity uS/cm) X 0.65 = TDS,[28] places the values for TDS in the reservoir between 22,737 mg/l, in the beginning, and 150,488 mg/l at the end. These values are within the range (800mg/l-300,000 mg/l) found in produced water from hydraulic fracturing operations.[16]

The FO samplers are easier to construct and less expensive than the Alzet samplers because they use less expensive membranes and housing components that do not require precision machining (appendices A-E). However, their use is likely limited to shallow environments, as they may not withstand high temperature and pressure. The thermoplastic housing of these samplers is subject to degradation under extreme conditions. Further testing is needed to establish the upper pressure and temperature limits that this design can withstand. In the study of hydraulic fracturing fluids, the FO samplers are well suited for deployment in storage ponds and tanks on the surface. Sampling at depth in a borehole may require a sampler constructed using stronger materials, similar to the Alzet sampler built for this test. This is assuming that the problem of inconsistent flux rate is solved. Other Alzet driven samplers have proven themselves in deep ocean applications and the higher strength materials and precision machining of this design would ensure continued operation in the extreme conditions found in a fracking borehole.

The variable flux rate observed in the Alzet sampler may have been caused by a small leak around one of the membranes. If this were the case and D.I. water was bypassing the

membrane, the flux rate would initially be very high, until the system approached equilibrium at which point it would slow. As the system approached equilibrium, D.I. water from the coil would be drawn into the now salty D.I. chamber of the sampler. This failure could have been the result of the holes in the support plate having been machined outside of tolerance. With the holes bored too large, sealing at each membrane relied entirely on the epoxy. Others who have constructed osmosamplers of this design recommended the Loctite epoxy I used.[29] Unfortunately, this epoxy has a watery consistency and has a long cure time making it unsuitable to fill large gaps. In the future, I would use the same G and S polymer used in the FO samplers as it has higher viscosity and successfully sealed the FO membranes.

The choice of materials for the vent hole plug in the FO samplers is also important. While inside the D.I. chamber of the pump, the grade 5 bolt rusted. As it did, the rust built up on the membrane. This may have begun to limit flow later in the test, but the effect was not noticeable in the data. A non-corrosive material, such as stainless steel or plastic, will be used for this plug in future samplers. The rust scale is concentrated on the membrane where it had not been epoxied offering an unexpected benefit for this test by proving that sealing off areas of the membrane with epoxy is an effective way to control membrane surface area.

During most deployments, the osmosampler will be fully submerged in the fluid it is sampling. Hydraulic fracturing fluids contain acids, such as HCl, and hydrocarbons which could slowly break down certain plastics over a multiple month deployment. Testing is necessary to assess the ability of ABS to chemically withstand hydraulic fracturing fluids. If ABS breaks down in the fluid, samplers of the same design could be constructed using polyvinyl chloride (PVC) pipe, which is also readily available and is resistant to different chemicals than ABS. If both PVC

and ABS were attacked by some component in fracking fluids, the design could be modified to use polypropylene (PP) or polyvinylidene fluoride (PVDF) pipe. These materials offer much higher chemical resistance, but are slightly more expensive and cannot be cemented together. All joints would have to be threaded or plastic welded, which complicates the construction process, but would allow for easier modification, and repetitive assembly and disassembly.

Flux rates in the pumps increase as the surrounding temperature increases. As a result, samples collected while the temperature is high will occupy a longer section of tubing than samples collected while the temperature is cooler. To account for this, samplers deployed in the field should have integrated temperature loggers. A temperature log will allow for the sample volume data to be adjusted based upon the changes in pump speed. In order to ensure accurate scaling of the data from the FO samplers based on the temperature log, a calibration curve will be needed. To construct this curve, a series of flux rate measurements should be obtained while varying the temperature in a temperature-controlled environment. This may have to be done in two stages, the first in a refrigerator to measure flux rates below room temperature, and the second in an incubator to measure flux rates above room temperature.

In this test, a temperature logger was included in the Alzet sampler, but was improperly programmed and did not record temperature data for more than 4 days of the study. Temperature could have resulted in variable flux mates in the three samplers used in this test, but the effect is minimal over the timescale of the experiment. The data collected for the Alzet and FO_1 samplers in this study represent averages over multiple days. Diurnal changes in temperature between night and day were the biggest swings in temperature experienced by the samplers during the test. Average data over multiple days includes these swings. Diurnal

changes in temperature may have affected the placement of the FO_2 sampler data on the overall timeline, but this data was scaled based on the values retrieved from the sampler rather than an expected timeline. Future studies will take temperature into account.

To date, studies of hydraulic fracturing fluid composition have relied on periodic sampling on the order of days to weeks. Periodic samples provide a snapshot of fluid conditions at a specific moment, but changes that occur between spot samples are missed entirely.[24] Osmosamplers show potential as a method to fill gaps in the dataset between spot samples. In this study, the FO_2 sampler was able to collect samples with 8-hour resolution. A sampler built with minor modifications to this design could provide resolution on the order of 1-hour. Hourly resolution could offer deeper insight into the mechanisms by which potentially hazardous shale constituents are mobilized and transported to the surface in produced water. Osmosamplers have the potential to provide high-resolution data regarding changes in the microbial community as a result of, or a cause of changes in fracking fluid chemistry. This information would be valuable to drilling companies to improve drilling practices, especially biocide usage, and regulatory agencies to improve monitoring.

The use of hydraulic fracturing as a means for natural gas extraction is rapidly expanding and the volume of wastewater from fracking wells is already overwhelming the treatment system that is in place.[18] A multifaceted approach is required to reduce the negative impact of increasing volumes of hydraulic fracturing waste. Any effort to improve recycling and treatment techniques will be rooted in data regarding the chemistry and microbiology of the fluids. By improving the understanding of how produced water becomes the transport medium for high concentrations of shale constituents, osmosamplers could provide the insight necessary to

develop new methods to remove those constituents in treatment plants, or minimize their initial mobilization into the fluids.

Through this research I developed a new design for an osmosampler which provides high resolution data regarding changes in fluid conditions over time. These samplers are significantly less expensive and easier to produce than their deep-sea counterparts. Any researcher with access to basic tools could construct samplers based on this design and deploy them in the field in a short period of time. Their low cost allows for a larger number of them to be built and deployed at a research site, granting spatial as well as temporal resolution. Furthermore, because osmosamplers are driven entirely by osmosis and do not require electrical power, they can deployed easily in remote areas. This capability would be a benefit to researchers in a number of fields. For example, osmosamplers using Alzet membranes have been used effectively to track nutrient fluxes in river systems.[24] Using osmosamplers, Gkritzalis-Papadopoulos et al. found that a large influx of nutrients occur in a matter of hours as a result of runoff during heavy rain events. The 24-hour spot sampling regime previously used in their research did not reflect these nutrient spikes and only with the use of continuous sampling through osmosamplers were they able to correct the nutrient budgets for their research site.[24]

The FO samplers do have some limitations and would be best used in augmenting existing spot sampling regiments rather than replacing them entirely. Osmosamplers collect small volumes of fluid, milliliters per time-point, whereas the sample volume collected through spot sampling is often liters per time-point. Osmosamplers store samples until they are retrieved, often days or weeks later. If the sample is not preserved properly, chemical reactions or trophic interactions, through nutrient uptake or predation, may occur within the tubing

resulting in data that does not represent the actual conditions in the sample environment. In contrast, spot samples can be processed as quickly as they can be transported to the lab. Furthermore, spot samples provide a precise snapshot of fluid conditions at a single moment. An osmosampler designed for daily resolution would provide data that is an average of the conditions over that day.

If used in conjunction with spot sampling, osmosamplers can fill temporal gaps between spot samples and offer insight into changes in fluid conditions that would otherwise be missed by spot samples. Spot samples can provide a timeline to help scale the osmosampler data. The low cost and ease of construction demonstrated through this research suggests that a simple osmosampler design can increase the value of this powerful data collection technique in field applications including the monitoring of fluids associated hydraulic fracturing and potentially beyond.

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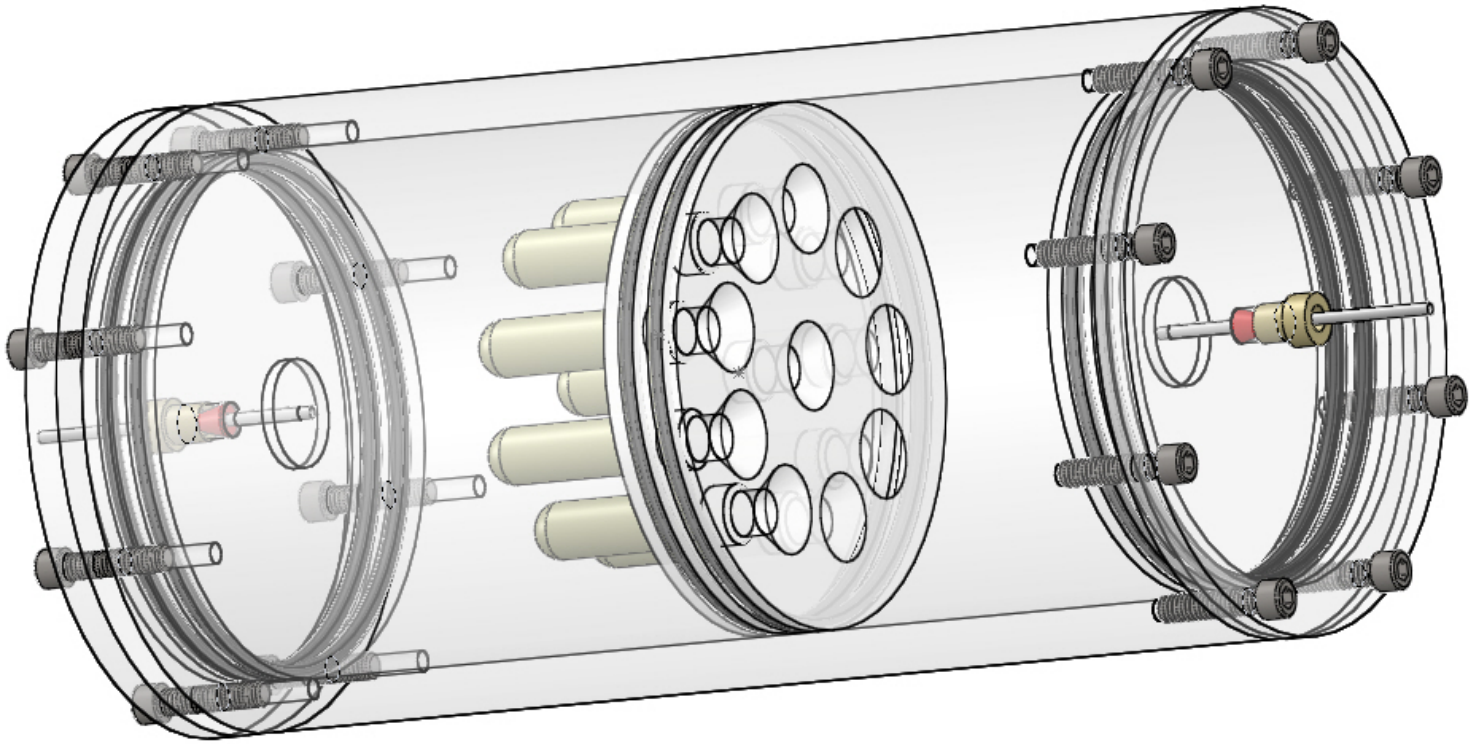
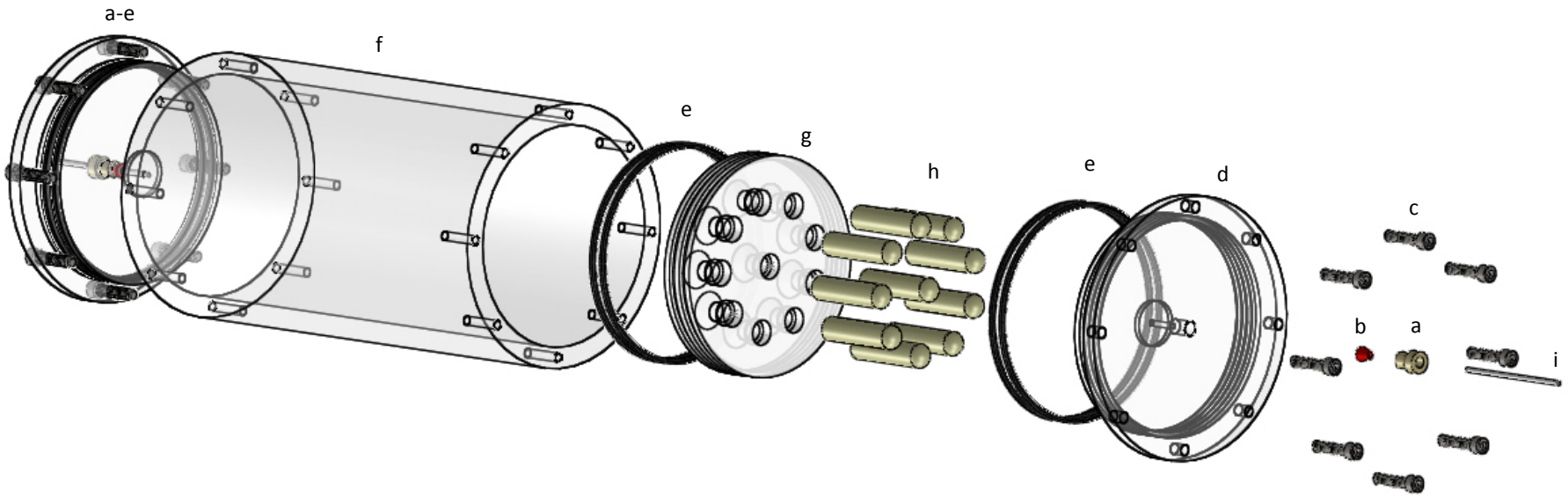
Appendix A: Drawing of Assembled Osmotic Pump using Alzet Membranes.

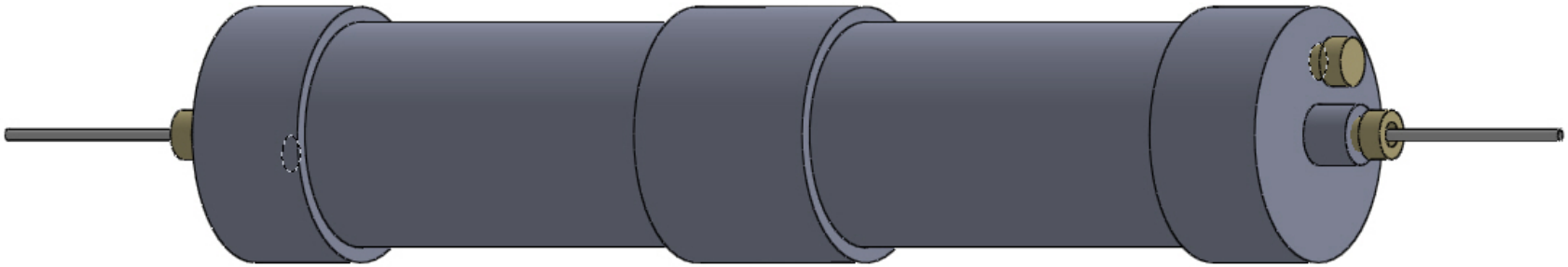


Appendix B: Exploded View of Osmotic Pump using Alzet Membranes.

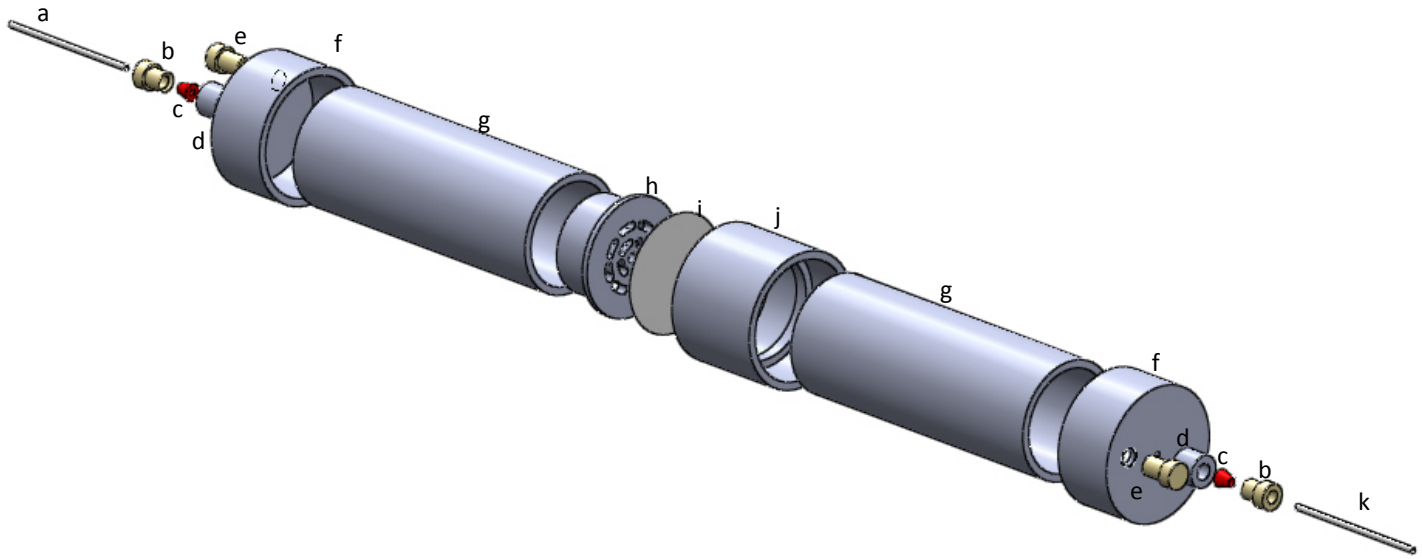


Pump Components: **a**. IDEX P-354 nut (x2); **b**. IDEX P-363r ferrule (x2); **c**. ¼”x1¼” stainless steel socket head machine screw (x12); **d**. 1” thick acrylic end cap with screw holes, inlet/outlet hole and 2 O-ring grooves; **e**. Viton Fluoroelastomer O-rings (McMaster-Carr part# 9464K126) (x6); **f**. 12” long section of 5/8” wall acrylic tubing with 6 x 1” ¼”-20 holes drilled per side; **g**. 1” thick membrane support with 10 membrane holes and 2 O-ring grooves **h**. Alzet 2ML1 membrane cartridges (x12); **i**. sample coil of 1mm ID Teflon tubing.

Appendix C: Drawing of Assembled Osmotic Pump using Porifera Membrane.



Appendix D: Exploded View of Osmotic Pump using Porifera Membrane.



Pump Components: **a**. 1mm ID Teflon outlet tubing; **b**. IDEX P-354 nut (x2); **c**. IDEX P-363r ferrule (x2); **d**. 1/2"x 5/8" spacer w/ drilled and tapped 3/8" hole (x2); **e**. IDEX P-311 plug (x2); **f**. 2" ABS pipe cap w/ 1/8" hole drilled in center and 3/8" tapped hole offset (x2); **g**. 6" length of 2" diameter schedule 40 ABS pipe (x2); **h**. 2" ABS flush pipe drain; **i**. 2" circle of Porifera membrane; **j**. 2" ABS pipe coupler; **k**. sample coil of 1mm ID Teflon tubing.

Appendix E: Cost Breakdown for Samplers using Porifera Membranes.

Part	Source	Part #	Cost/Unit ($)	Quantity	Sub Total ($)	Description
Teflon Tubing	Zeus Inc.	AWG17 SW Teflon FEB tubing	0.48	250	120	The amount of tubing needed will depend on the duration of sampler deployment, the desired resolution and the volume of sample needed per time point. Units in feet.
Nuts	IDEX	P-354	1.3	2	2.6	1/4-28 TEFZEL (ETFE)
Ferrules	IDEX	P-363r	1.26	2	2.52	2mm TEFZEL (ETFE)
Vent Plugs	IDEX	P-311	1.9	2	3.8	1/4-28 TEFZEL (ETFE)
2” ABS Pipe	Home Depot		1.35	2	2.7	6" length
2” ABS Caps	Home Depot		4.73	2	9.46	
2” ABS Drains	Home Depot		1.75	1	1.75	
2” ABS Couplers	Home Depot		0.99	1	0.99	
ABS Cement	Home Depot		8.27	0.0625	0.516875	16 oz can
ABS Stock	Hytec Plastics		178.43	0.001736111	0.309774306	Cost/Unit is per 24"x24" sheet
Paint	Home Depot		5.98	0.25	1.495	Plastic spray paint or waterproof latex paint to add protective layer to samplers
Membrane Adhesive	GS Polymers	gsp-1541	12	0.25	3	
Dispenser Mixing Tips	GS Polymers	SM5.3/24	0.75	1	0.75	
Membrane Material	Porifera		N/A			
Temperature Loggers	Maxim Integrated	DS1922L	52.02	1	52.02	May not need to be installed in every sampler
Temperature Logger Housing	Maxim Integrated	DS9017+	30	1	30	May not need to be installed in every sampler
				Total:	231.91	
				Pump cost w/o tubing.	111.91	
				Pump cost w/o tubing and temp logger.	29.89	